Ocean acidification off the south coast of Japan: A result from time series observations of CO_2 parameters from 1994 to 2008

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[1] Ocean acidification resulting from increases in present and future atmospheric CO_2 levels could seriously affect diverse coastal and oceanic ecosystems. In this work, we determine that a significant trend in ocean acidification is superposed on the large seasonal and interannual variabilities of acidity in surface waters off the south coast of Honshu, Japan, based on our repeated observations of partial pressure of CO_2 (pCO_2), total inorganic carbon (TCO_2), and pH. Multiple regression analysis of TCO_2 as a function of temperature, salinity, and timing of observations shows that TCO_2 increased at a rate of $+1.23 \pm 0.40$ μmol kg^{-1} yr^{-1} for the period 1994–2008, while no long-term change has been determined for total alkalinity calculated from TCO_2 and pCO_2 in seawater. These results indicate that pH and the aragonite saturation state (Ω_{arag}) are decreasing at a rate of -0.020 ± 0.007 decade^{-1} and -0.12 ± 0.05 decade^{-1}, respectively. If future atmospheric CO_2 levels keep increasing as predicted by the Intergovernmental Panel on Climate Change emission scenario A1FI, which postulates intensive fossil fuel use associated with very rapid economic growth, a further reduction of -0.8 to -1.0 in Ω_{arag} is likely in the next 50 years. Such a rapid reduction of Ω_{arag} could have negative impacts on a variety of calcareous organisms.

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1. Introduction

[2] Long-term increases of CO_2 levels in seawater and the atmosphere have been observed in various oceanic zones such as subtropical North Pacific and North Atlantic [e.g., *Inoue et al.*, 1995; *Midorikawa et al.*, 2005; *Takahashi et al.*, 2006; *Bates*, 2007; *Dore et al.*, 2009], the equatorial Pacific [e.g., *Feely et al.*, 2006; *Ishii et al.*, 2009], subarctic North Pacific and North Atlantic [e.g., *Schuster et al.*, 2009; *Metzl et al.*, 2010; *Wakita et al.*, 2010; *Wong et al.*, 2010] and the Southern Ocean [*Inoue and Ishii*, 2005; *Takahashi et al.*, 2009; *Metzl*, 2009]. Although it is important to understand the changes in ocean circulation, biogeochemical processes and their roles in changing oceanic CO_2 levels, the long-term CO_2 increase in the ocean is predominantly attributable to the absorption of CO_2 that is rapidly increasing in the atmosphere, primarily as a result of human activities such as fossil fuel combustion and land-use changes.

[3] The absorption of CO_2 by the ocean is chemically equivalent to the addition of carbonic acid to seawater. It is evident that the addition of carbonic acid raises the hydrogen ion concentration ([H$^+$]) and lowers carbonate ion concentration ([CO_3^{2-}]), thus lowering the degree of calcium carbonate ($CaCO_3$) saturation of seawater. These changes in carbonate chemistry, commonly referred to as ocean acidification, may seriously affect marine organisms and ecosystems throughout the oceans [*Doney et al.*, 2009]. It is presumed that the ocean acidification has been in progress not only in open oceans where long-term increases in CO_2 have been observed but also in coastal zones through the air-sea CO_2 exchange and mixing with waters from offshore open zones. In addition to habitat loss, water pollution, eutrophication, and overexploitation, ocean acidification may be another human-induced threat to coastal marine ecosystems and sustainable fisheries. However, little is known about the progress of acidification in coastal oceans at present [*Santana-Casiano et al.*, 2007; *Feely et al.*, 2008].

[4] In this study, we focus on the coastal ocean between the south coast of Honshu, Japan, and the Kuroshio (Figure 1), and investigate the trend of ocean acidification on the basis

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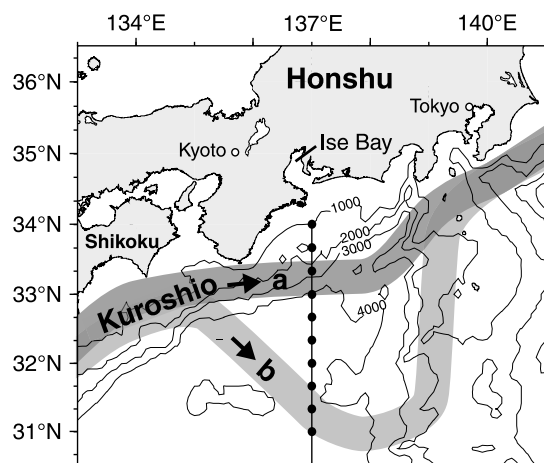
Figure 1. Repeat stations along 137°E in the vicinity of the Kuroshio off the south coast of Honshu, Japan. Also shown are the approximate positions of the nearshore nonlarge meander path (point a) and offshore large meander path of the Kuroshio (point b).

of the time series data of seawater CO_2 parameters from samples collected near the surface. In contrast to the oligotrophic open subtropical zone south of the Kuroshio, the studied region in the northern side of Kuroshio is characterized by higher primary productivity ($>$200 gC m^{-2} yr^{-1}) [*Yokouchi et al.*, 2006] with high biomass of diatom (80–270 mg m^{-2} in euphotic layer) in spring phytoplankton bloom [*Sugisaki et al.*, 2010]. This is also an important spawning region for many species of pelagic fish such as sardine and mackerel. Owing to the close proximity to densely populated regions in Japan, the fish catch and the crop of aquaculture in this zone amounted to 470,000 tons in 2009 (see http://www.maff.go.jp/j/tokei/kouhyou/kaimen_gyosei/index.html). In regard to calcareous organisms, the crop of aquaculture on the coast included 5000 tons of oysters and 2 tons of pearls. This region is also known as a habitat of a cocolithophore *Gephyrocapsa oceanica*. Its massive bloom sometimes develops extensively in late spring [e.g., *Kai et al.*, 1999]. The south coast of Honshu is also the northern limit of tropical reef corals' habitat in the North Pacific [*Yamano et al.*, 2011].

[5] Trend in pCO$_2$sw in the northern side of Kuroshio is also quite different from that in the south. Shipboard underway measurements of partial pressure of CO_2 in surface seawater (pCO$_2$sw) and in the overlying atmosphere (pCO$_2$air) have been made every winter (January–February) since 1983 from 3°N through 34°N along 137°E [*Inoue et al.*, 1995; *Midorikawa et al.*, 2005]. In the southern side of Kuroshio, the mean rate of pCO$_2$sw increase for each 1° in latitude between 22°N and 30°N ranged from +1.48 ± 0.10 to +1.70 ± 0.12 μatm yr^{-1} for 1983–2007. These rates were not significantly different from the rate of increase in pCO$_2$air (+1.63 ± 0.04 to +1.70 ± 0.03 μatm yr^{-1}) [*Midorikawa et al.*, 2010]. These findings strongly suggest that the surface waters in the open subtropical zone are being acidified as a result of net transfer of anthropogenic CO_2 into the ocean. The rate of pH decrease has been calculated to be −0.019 ± 0.001 to −0.021 ± 0.002 decade^{-1}. In the northern side of Kuroshio at around 34°N above conti-

nental slope $\sim$25 km off the coast, the long-term increase in pCO$_2$sw has also been observed in winter (+1.78 ± 0.50 μatm yr^{-1}). However, the interannual variability in pCO$_2$sw (±14.6 μatm) was about three times as large as that in the southern side (±3.4 to ±5.4 μatm). Owing to this large interannual variability, the uncertainty (standard error) in the rate of pCO$_2$sw increase (±0.50 μatm yr^{-1}) is three to four times as large as that in the south. Sea surface temperature (SST) at 34°N also showed larger interannual variability (16.7 ± 1.4 (1s) °C) than those in the south (e.g., 20.0 ± 0.5°C at 30°N). When thermodynamic effects of SST change, +4.0% °C^{-1}, and salinity change, +4.4% per salinity unit, were corrected, the rate of long-term increase in pCO$_2$sw was even more uncertain (+1.5 ± 1.0 μatm yr^{-1}) and statistically not significant (α = 0.05). For these reasons, the rate of pH decrease in the coastal ocean north of the Kuroshio at 34°N has not been evaluated from the time series data of pCO$_2$sw in winter.

[6] In this study, we investigate the seasonal and interannual variability in total dissolved inorganic carbon (TCO$_2$) and total alkalinity (TA) together with those in SST and salinity that control the variability in pCO$_2$sw and pH for the coastal ocean north of the Kuroshio. The long-term trends of TCO$_2$ and TA in surface water are determined by multiple regression analyses for the data that have been acquired since 1994. The rate of changes in pH and the saturation states of aragonite and calcite are determined from these results for changes in carbonate chemistry, and their future projections are discussed.

2. Materials and Methods

[7] Oceanic and atmospheric CO_2 observations have been repeated together with the hydrographic/hydrochemical observations in the western North Pacific along 137°E onboard the Japan Meteorological Agency's research vessels *Ryofu Maru* and *Keifu Maru*. The frequency of observations has changed from annually each winter in the 1980s, to biannually each winter and summer in the 1990s and early 2000s although TCO$_2$ measurements were made at irregular intervals (Figure 2), to each season since 2003.

[8] Underway measurements of pCO$_2$sw and pCO$_2$air have been made since 1983 using an automated CO_2 analyzer equipped with a nondispersive infrared (NDIR) gas analyzer, a showerhead equilibrator and four CO_2 standards in air. Details of the method have been described by *Inoue* [2000] and *Midorikawa et al.* [2006]. Seawater was pumped up continuously from the bottom of the ship ($\sim$5 m below sea level) and introduced into the equilibrator for pCO$_2$sw measurements. We think that the error in pCO$_2$sw data is ±2 μatm. This is primarily ascribed to the uncertainty (±0.1°C) in measuring the temperature change of water in the inner piping from the water intake to the equilibrator and its thermodynamic effect on pCO$_2$sw (about +4.0% °C^{-1}). The data of pCO$_2$ obtained by JMA are available from the World Data Centre for Greenhouse Gases (WDCGG; http://gaw.kishou.go.jp/wdcgg/). They have also been stored in LDEO Database V2009 [*Takahashi et al.*, 2010] (http://cdiac.ornl.gov/oceans/LDEO_Underway_Database/) and Surface Ocean Carbon Atlas (SOCAT) Database (http://cdiac.ornl.gov/oceans/SOCAT/).
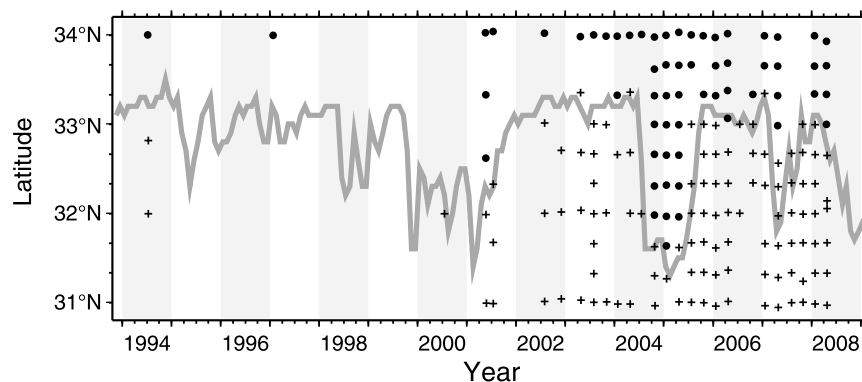
Figure 2. Time series of the southernmost latitude of the Kuroshio axis at 136°–140°E (http://www.data.kishou.go.jp/shindan/b_2/kuroshio_stream/kuroshio_stream.html) and time-latitude distributions of total dissolved inorganic carbon (TCO$_2$) data along 137°E in the north (circles) and the south (crosses) of the Kuroshio.

[9] Since 1994, TCO$_2$ has been measured using a CO$_2$ extraction–coulometry method [*Ishii et al.*, 1998], and since 2003, pH has been measured using an indicator dye–spectrophotometry method in total hydrogen ion concentration scale ($\approx -\log_{10}\{([H^+]_F + [HSO_4^-])/\mu$mol kg$^{-1}\}$) at 25°C (pH$_{T25}$) [*Saito et al.*, 2008]. Samples for TCO$_2$ and pH$_{T25}$ analyses were taken from the water that was continuously pumped up for pCO$_2$sw measurement or water taken at 5 m below sea surface with Niskin bottles on CTD/carousel multi sampler. They have been sampled in 250 cm^3 borosilicate glass bottles with ground glass stoppers lubricated with Apiezon L grease. For the majority of cruises, samples were poisoned with mercury(II) chloride and analyzed in the laboratory on land after the cruise. During some cruises, samples were measured onboard immediately after collection. In July 1994, samples for TCO$_2$ have also been collected at depths from the surface to near bottom at some stations around the Kuroshio as a part of World Ocean Circulation Experiment Hydrographic Program P09 one-time cruise, and they were analyzed immediately after sampling on board. To establish the identical concentration scale among cruises, we used numbers of batches of Certified Reference Material (CRM) for TCO$_2$ and TA analyses provided by *Dickson* [1991] and *Dickson et al.* [2003] (http://andrew.ucsd.edu/co2qc/index.html) for quality control. Certified values of TCO$_2$ and TA were used to calculate the reference value of pH$_{T25}$ for quality control of pH$_{T25}$ measurements. We used dissociation constants for carbonic acid given by *Lueker et al.* [2000] as recommended by *Dickson et al.* [2007] in all calculations of carbonate chemistry in seawater. We also prepared a lot of batches of reference seawater in a similar method to that of *Dickson* [1991] from the oligotrophic surface waters in western North Pacific, and calibrated its TCO$_2$ and pH$_{T25}$ with the CRM. Before and after each run of analyses (usually 20 to 30 samples in each run), either CRM or reference seawater was also analyzed. The precision of analysis is smaller than ± 2 μmol kg^{-1} for TCO$_2$ and smaller than ± 0.002 for pH$_{T25}$.

[10] The value of TA was calculated from pCO$_2$sw, TCO$_2$, SST and salinity for 1994–2008. Its repeatability is estimated to be ± 3 μmol kg^{-1} from the precisions of pCO$_2$sw and TCO$_2$ measurements. For 2003–2008, the value of TA was also calculated from pH$_{T25}$, TCO$_2$ and

salinity at 25°C. The differences in TA values calculated from these pairs of CO$_2$ parameters were 2.4 ± 3.0 μmol kg^{-1} (mean $\pm 1s$; $n = 62$) for samples collected from 32°N to 34°N. *Midorikawa et al.* [2010] also showed that pH$_{T25}$ measured with spectrophotometry and that calculated from pCO$_2$, TCO$_2$, SST and salinity also agreed well. Their difference averaged 0.0026 ± 0.0050 (mean $\pm 1s$) in winters of 2003–2008, supporting the internal consistency of CO$_2$ parameters when the dissociation constants given by *Lueker et al.* [2000] was used for calculations. We also calculated pH at SST from pH$_{T25}$, TCO$_2$, SST and salinity, and the saturation state (Ω) for both naturally occurring crystal forms of calcium carbonate, aragonite and calcite, using their apparent solubility products K'_{sp} [*Mucci*, 1983]:

$$\Omega = [Ca^{2+}][CO_3^{2-}]/K'_{sp}. \tag{1}$$

3. Oceanographic Setting

[11] The Kuroshio is the western boundary current in the subtropical zone of the western North Pacific. At around 137°E, it usually flows due eastward at around 33°10′N above the continental rise (nearshore nonlarge meander path) (Figures 1 and 2). However, it sometimes takes offshore large meander paths [*Kawabe*, 1985]. One of the remarkable meanders has occurred in August 2004 and continued until July 2005 for 1 year. In this period, the strongest part of the Kuroshio, the Kuroshio axis, that is conventionally defined as the latitude where the 15°C isotherm intersects the 200 m isodepth [*Kawai*, 1969], has been steadily located south of 32°N and moved even further south to 31°20′N in February 2005 (Figure 2) (http://www.data.kishou.go.jp/kaiyou/db/kaikyo/series/junkro.html). Consequently, the locations of sampling stations at 31°40′N through 33°20′N moved back and forth between the southern and the northern sides of the Kuroshio depending on its path for 1994–2008. In contrast, the stations at 33°40′N and 34°00′N that are located nearshore above the continental slope have always been on the northern side of the Kuroshio.

[12] The Kuroshio is a geostrophic current, and the depths of isotherms and contour lines of other physical and chemical parameters change largely across the Kuroshio
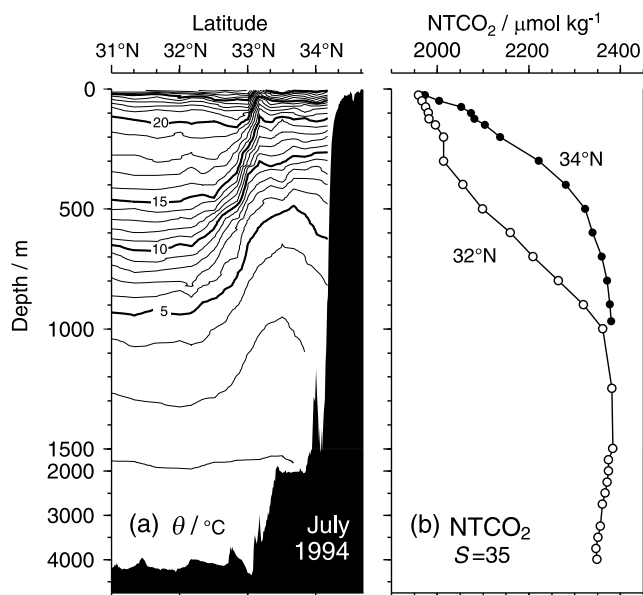
Figure 3. (a) Vertical section of potential temperature between 31°N and 34°N and (b) vertical profiles of salinity-normalized TCO_2 ($S = 35$) at 32°N and 34°N along 137°E in July 1994 during the World Ocean Circulation Experiment P09 cruise. Data are available from the Climate Variability and Predictability program and the Carbon Hydrographic Data Office (http://cchdo.ucsd.edu/pacific.html).

(Figure 3a) [*Kaneko et al.*, 1998]. For example, in July 1994 when the Kuroshio took a nearshore nonlarge meander path, the 15°C isotherm lay at the depth of ~450 m in the southern offshore side, but it lay at ~120 m in the northern nearshore side. The mixed layer in winter can reach 150 m below surface (Figure 4) in the north while it can reach 200m in the south. Accordingly, mean SST in midwinter (early March) is significantly lower in the north than in the south (+14.9 ± 1.3°C and +19.1 ± 0.5°C in 1° × 1° pixel centered at 137.5°E, 34.5°N and 137.5°E, 30.5°N for 1994–2008, respectively).

[13] The vertical profiles of TCO_2 as well as other chemical components also differ largely between the southern and the northern sides. In the north, the vertical gradient of TCO_2 in the top 500 m is much steeper than in the south (Figure 3b). In July 1994, $NTCO_2$ at the depth of 100m, which is thought to be near the bottom of the mixed layer in the preceding winter, was 2074 μmol kg^{-1}. It was more than 100 μmol kg^{-1} higher than in the surface (1970 μmol kg^{-1}) and suggests the importance of vertical mixing in raising the $NTCO_2$ in surface water in winter.

[14] Direction of coastal current changes with time (http://www.data.kishou.go.jp/kaiyou/db/kobe/jun/current_k.html). When Kuroshio takes offshore large meander path, a westward current prevails at around 34°N due to the cyclonic eddy formed in the interior of the meander path [e.g., *Rikiishi*, 1974; *Kamachi et al.*, 2004], and this region becomes rather warmer [*Sugimoto and Yoshida*, 2005] (Figure 4). It has also been recognized that the oceanic water in the off of south coast intrudes into the adjacent coastal basins such as Ise Bay by tidal current [*Kasai et al.*, 2004]. Intrusion of the oceanic water greatly affects physical, chemical and biological properties in the coastal basins.

4. Results

4.1. Seasonal and Interannual Variations

[15] The coastal ocean south of Honshu is a strong sink for atmospheric CO_2, as is the same latitudinal zone in the open western North Pacific around the Kuroshio Extension [*Takahashi et al.*, 2009]. In spring, pCO_2sw usually shows the lowest values that are about 80 μatm lower than pCO_2air (Figure 5a). In summer, pCO_2sw tends to show the highest values that are comparable to pCO_2air. Also note that, in fall and winter, pCO_2sw shows large interannual variability. For example, pCO_2sw at 34°N was 314 μatm in January 2005 and 362 μatm in January 2006.

[16] These large seasonal and interannual variations in pCO_2sw are attributable to large variations in SST (+13.7 to +27.6°C) and salinity-normalized TCO_2 ($NTCO_2$) (1969 to 2088 μmol kg^{-1} at $S = 35$; Figures 5b and 5f). In general, $NTCO_2$ increases as SST decreases, but their relationship varies among SST domains (Figure 6). In warm seasons (+23°C < SST) when pCO_2sw varies widely (315 to 384 μatm), variations in $NTCO_2$ are relatively small (1969 to 1991 μmol kg^{-1}), and the thermodynamic effects of temperature changes (about +4.0% °C^{-1}) mainly control the variation of pCO_2sw. In the SST range from 16.5°C to 21.5°C, when pCO_2sw is the lowest (275 to 322 μatm), the change in $NTCO_2$ is large (1981 to 2029 μmol kg^{-1}) and its effect on pCO_2sw compensates for the thermodynamic effect of temperature change. Consequently, pCO_2sw is apparently insensitive to changes in SST. In the coldest time (SST < +16°C), the effect of the change in $NTCO_2$ (2042 to 2088 μmol kg^{-1}) becomes dominant, and pCO_2sw increases as SST decreases. The marked increase in $NTCO_2$ causes the increase in pCO_2sw in winter (Figure 5a), and the large interannual variability of pCO_2sw in winter is mainly ascribed to the large interannual
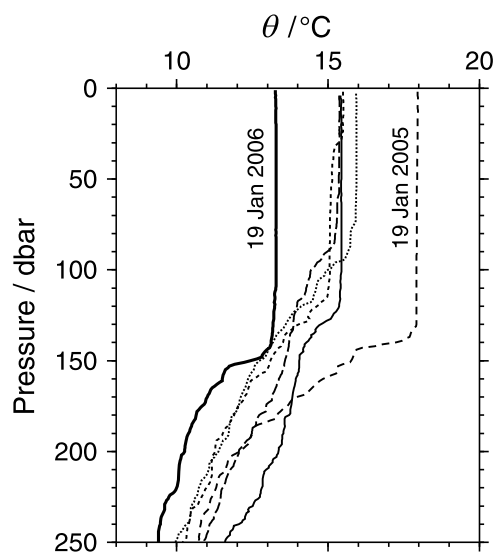

Figure 4. Vertical profiles of temperature at 137°E, 34°N observed in each January of 2003–2008.

variability of $NTCO_2$ that is closely related to the variability of SST.

[17] The pH_{T25} is lower (7.90 to 7.94) in winter and higher (8.08 to 8.16) in summer (Figure 5c). This seasonality is opposite that of $NTCO_2$. In contrast, salinity-normalized total alkalinity (NTA) calculated from pCO_2sw and TCO_2, or TCO_2 and pH_{T25}, together with temperature and salinity shows very small variation (Figure 5d). The mean value of NTA calculated from pCO_2sw and TCO_2 is 2305.1 ± 5.0 μmol kg^{-1} ($n = 52$), which is significantly higher than in the south of Kuroshio (2295.1 ± 5.2 μmol kg^{-1}; $n = 159$) calculated in the same method [*Midorikawa et al.*, 2010]. These results indicate that changes in pH_{T25} are tightly coupled to changes in $NTCO_2$. The controlling factors of seasonal $NTCO_2$ variation are yet to be quantified, but are

possibly ascribed to the vertical mixing in fall and winter, net biological CO_2 uptake in winter and summer, and net air-sea CO_2 exchange as in the south of the Kuroshio [*Ishii et al.*, 2001].

[18] In contrast to the seasonal variation of pH_T measured at 25°C, pH at in situ temperatures (pH_{TSST}) tends to be higher (8.14–8.18) in winter and spring, and lower (~8.06) in summer (Figure 5c). As for pCO_2sw, such a seasonal variation in pH_{TSST} is attributable to variations in SST and $NTCO_2$. In warm seasons, the increase in SST has a large thermodynamic effect on carbonate chemistry and elevates the concentration of hydrogen ion in seawater.

[19] The seasonality of Ω is similar to that of pH_{T25} rather than of pH_{TSST} (Figure 5e). In summer, saturation state of aragonite (Ω_{arag}) reaches its maximum value of about 3.8, but it decreases in winter to less than 3.0. Note that Ω_{arag} dropped to 2.45 in January 2006 when conditions of low SST (13.7°C), high $NTCO_2$ (2088 μmol kg^{-1}), and low pH_{T25} (7.905) were observed at the sampling site of 34°N.

4.2. Multiple Regression Analysis for Long-Term Trends

[20] In this study, we applied multiple regression analysis to $NTCO_2$ data from measurements and NTA data calculated from pCO_2sw and TCO_2 in surface water. The observed $NTCO_2$ was fitted as an empirical function of timing of observation (yr) and physical parameters such as temperature (SST) and salinity (SSS):

$$NTCO_2/\mu mol\,kg^{-1} = TCO_2 \cdot S^{-1} \cdot 35/\mu mol\,kg^{-1}$$
$$= f(yr, SST, SSS) = c_0 + c_1 \cdot yr + c_2 \cdot SST$$
$$+ c_3 \cdot SST^2 + c_4 \cdot SST^3 + c_5 \cdot SSS + \varepsilon,$$

$$(2)$$

where yr = year − 2000, SST = temperature/°C − 20.0, and SSS = salinity − 35.0. The terms c_0, c_1, c_2, c_3, c_4, and c_5 are coefficients of multiple regression, and ε represents the residual of the fitting. The polynomial of temperature (SST)
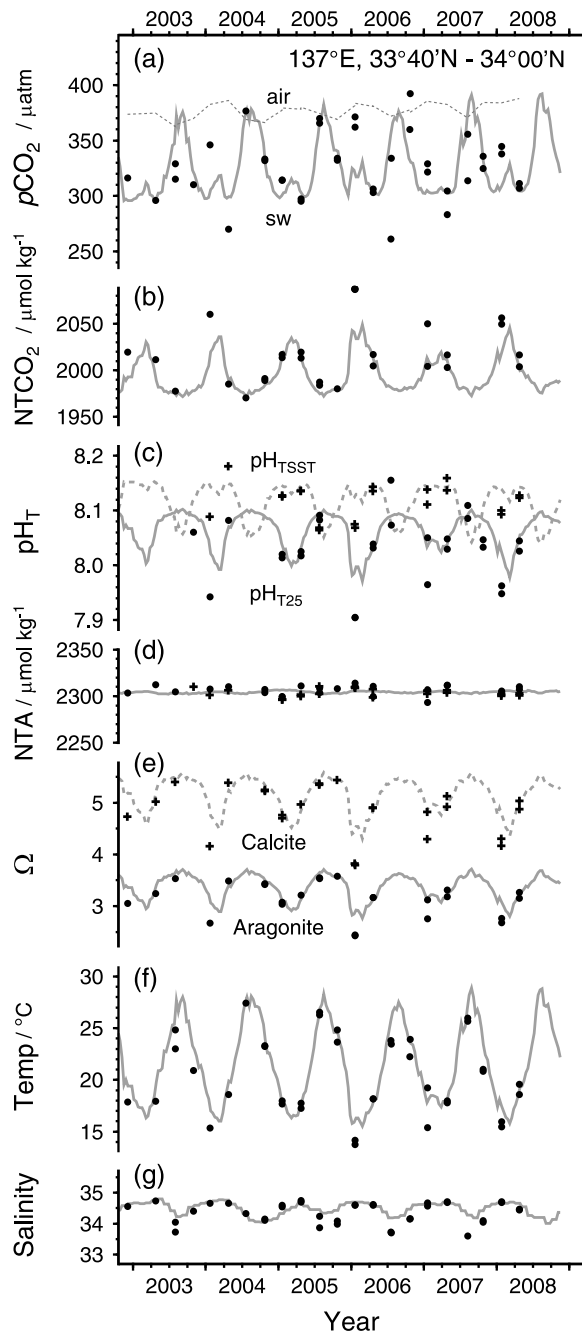

Figure 5. Time series of seawater CO_2 and hydrographic parameters in surface water of the coastal ocean south of Honshu, Japan (a composite of data at 137°E, 33°40′N–34°N), for December 2002–April 2008. (a) Partial pressure of CO_2 in seawater (pCO_2sw, circles) and in the atmosphere (dashed shaded line); (b) salinity-normalized total inorganic carbon at $S = 35$ ($NTCO_2$); (c) pH in total hydrogen ion concentration scale measured at 25°C (pH_{T25}, circles) and that calculated at SST from $NTCO_2$, pH_{T25}, sea surface temperature (SST), and sea surface salinity (SSS) (pH_{TSST}; crosses); (d) salinity-normalized total alkalinity at $S = 35$ (NTA) calculated from pCO_2sw, $NTCO_2$, SST, and SSS (circles) and NTA calculated from $NTCO_2$, pH_{T25}, SST, and SSS (crosses); (e) saturation state of aragonite (Ω_{arag}, circles) and calcite (Ω_{calc}, crosses); (f) SST; and (g) SSS. Also shown with solid shaded lines in Figures 5f and 5g is 10 day 1° × 1° mean SST (http://goos.kishou.go.jp/rrtdb/jma-pro.html) and monthly 1° × 1° mean SSS provided by data assimilation [*Usui et al.*, 2006], respectively. Solid shaded lines in Figures 5a–5e and dashed shaded lines in Figures 5c and 5e are the simulated time series data from 1° × 1° mean SST, SSS, and equations (3) and (5).
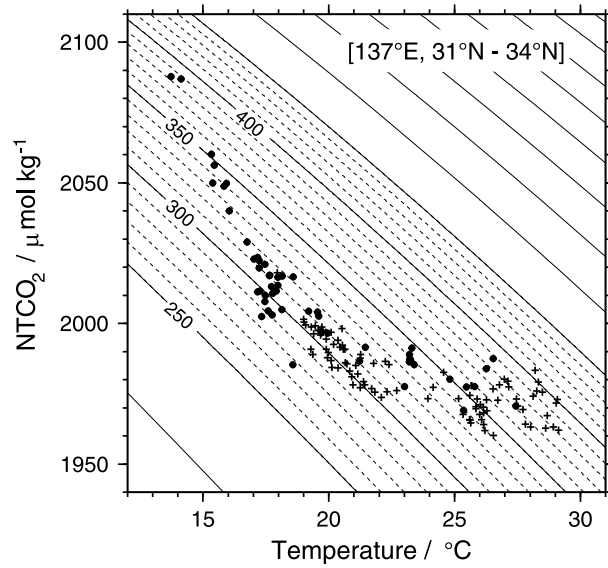
Figure 6. Temperature versus salinity-normalized total inorganic carbon at $S = 35$ (NTCO$_2$) in surface water at 137°E, 31°–34°N for December 2002–April 2008 in the north (circles) and south (crosses) of the Kuroshio axis. Contour lines show the pCO$_2$sw field calculated at a salinity of 34.5 (the average salinity for this region) and a salinity-normalized total alkalinity at $S = 35$ (NTA) of 2301 μmol kg^{-1} (the average NTA for this region).

in equation (2) exhibits the strong correlation between NTCO$_2$ and temperature in the seasonal, interannual, and spatial variations (Figure 6), and it is assumed that these regression coefficients did not change over the period of time series observations (1994–2008).

[21] For the coastal ocean between the south coast of Honshu and the Kuroshio in all seasons from July 1994 through April 2008, near-surface NTCO$_2$ was expressed as

$$
\begin{aligned}
\text{NTCO}_2/\mu\text{mol kg}^{-1} = {} & 1980.1(\pm 4.0) + 1.23(\pm 0.40) \cdot \text{yr} \\
& - 6.61(\pm 0.69) \cdot \text{SST} + 1.05(\pm 0.08) \cdot \text{SST}^2 \\
& - 0.072(\pm 0.019) \cdot \text{SST}^3 - 13.0(\pm 5.6) \\
& \cdot \text{SSS} + \varepsilon. \qquad (3)
\end{aligned}
$$

The standard errors are shown in parentheses, and the root mean square of ε was 6.6 μmol kg^{-1} ($n = 61$). The time series of seasonally detrended NTCO$_2$ at SST of 20°C and salinity of 35, i.e.,

$$
\begin{aligned}
\text{Seasonally detrended NTCO}_2 &= c_0 + c_1 \cdot \text{yr} + \varepsilon \\
&= 1980.1 + 1.23 \cdot \text{yr} + \varepsilon, \qquad (4)
\end{aligned}
$$

is shown in Figure 7. Spatial and interannual variations of NTCO$_2$ that accompany changes in SST and salinity in the same relationship as seasonal variation are also detrended with this process. The rate of linear increase in NTCO$_2$, i.e., the regression coefficient c_0 is $+1.23 \pm 0.40$ μmol kg^{-1} yr^{-1} ($n = 61$), and the 95% confidence interval is from +0.43 to
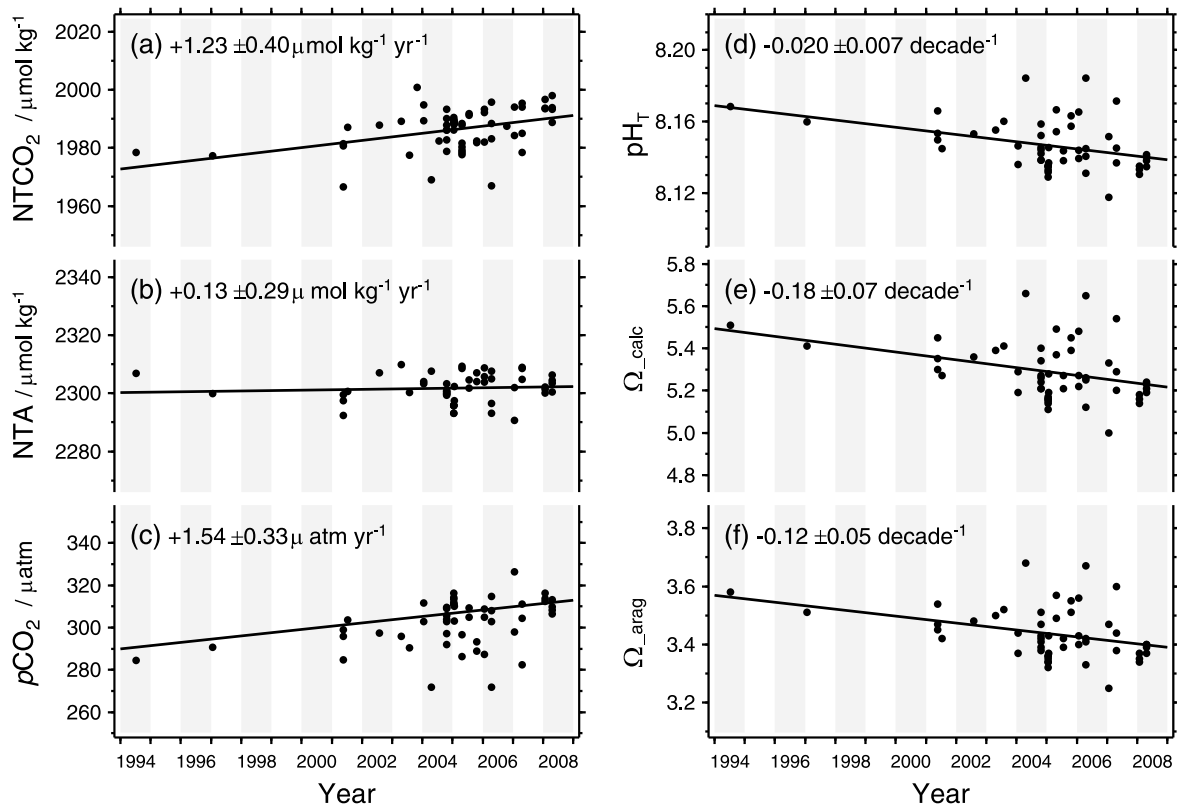

Figure 7. Seasonally detrended time series of (a) salinity-normalized total inorganic carbon at $S = 35$ (NTCO$_2$), (b) salinity-normalized total alkalinity at $S = 35$ (NTA), (c) partial pressure of CO$_2$ in seawater (pCO$_2$sw), (d) pH in total hydrogen ion concentration scale (pH$_T$), and (e) saturation state of calcite (Ω_{calc}) and (f) that of aragonite (Ω_{arag}) in surface water north of the Kuroshio axis at 137°E.

$+2.02$ μmol kg^{-1} yr^{-1}. The result indicates that NTCO$_2$ is increasing significantly in this region (Figure 7a). Note that there are some outlying data in spring. These outliers are indicative of the decoupling of NTCO$_2$ and temperature in spring when TCO$_2$ is decreasing due to spring biological production [*Yokouchi et al.*, 2006] while surface water is warming. However, when all spring data are excluded, the multiple regressions still indicate a significant increase in NTCO$_2$ at a rate of $+0.92 \pm 0.34$ μmol kg^{-1} yr^{-1} ($n = 37$). It is also noteworthy that the relationship between SST and NTCO$_2$ within and south of the Kuroshio overlaps those in the north (Figure 6). The multiple regressions for all NTCO$_2$ data in the north of 32°N regardless of the Kuroshio path gave the rate of increase of $+0.85 \pm 0.23$ μmol kg^{-1} yr^{-1} ($n = 122$) and the 95% confidence interval from $+0.39$ to $+1.32$ mol kg^{-1} yr^{-1}. This suggests that the rate of increase is not very sensitive to the choice of data near the Kuroshio axis.

[22] The observed near-surface NTA was also fitted as an empirical function of timing of observation (yr) and physical parameters:

$$NTA/\mu mol\,kg^{-1} = TA \cdot S^{-1} \cdot 35/\mu mol\,kg^{-1}$$
$$= c_0' + c_1' \cdot yr + c_2' \cdot SST + c_5' \cdot SSS + \varepsilon'$$
$$= 2301.1(\pm 2.8) + 0.13(\pm 0.29) \cdot yr$$
$$- 0.43(\pm 0.17) \cdot SST - 6.1(\pm 2.7) \cdot SSS + \varepsilon'.$$
(5)

The root mean square of ε' was 4.9 μmol kg^{-1} ($n = 52$). For NTA, however, the linear rate of increase of $+0.13 \pm 0.29$ μmol kg^{-1} yr^{-1} (Figure 7b) determined is not significant. Therefore, there is no evidence that NTA is increasing or decreasing in this zone. The time series of seasonally detrended NTA at SST of 20°C and salinity of 35, i.e.,

$$Seasonally\,detrended\,NTA = c_0' + c_1' \cdot yr + \varepsilon'$$
$$= 2301.1 + 0.13 \cdot yr + \varepsilon',$$
(6)

is shown in Figure 7. Anthropogenic airborne acid deposition and other acid pollutants potentially have a substantial impact on carbonate chemistry in seawater by reducing NTA [*Doney et al.*, 2007]. However, it is unlikely that they have a significant long-term impact in the coastal ocean we studied.

5. Discussion

[23] We calculated the rate of increase of pCO$_2$sw in the coastal ocean north of Kuroshio from the detrended NTCO$_2$ and NTA that is represented by (4) and (6) at SST of 20°C and salinity of 35, respectively. Seasonally and interannually detrended pCO$_2$sw thus calculated was increasing at a rate of $+1.54 \pm 0.33$ μatm yr^{-1} for 1994–2008 (Figure 7c). This rate agrees well with that of atmospheric pCO$_2$ increase ($+1.99 \pm 0.02$ μatm yr^{-1}) measured onboard for the same period. The rate of pH$_T$ change was also calculated in the same manner. It was -0.020 ± 0.007 decade^{-1} (Figure 7d) and is in good agreement with rates that have been determined in the central North Pacific near Hawaii (-0.019 ± 0.002 decade^{-1}) [*Dore et al.*, 2009] and the subtropical western North Pacific along 137°E in winter ($-0.015 \pm$

0.002 decade^{-1} to -0.021 ± 0.002 decade^{-1}) [*Midorikawa et al.*, 2010]. The concentration of carbonate ion in seawater is computed to be decreasing by $-3.2 \pm 0.7\%$ decade^{-1}. This decrease corresponds to the lowering of Ω_{calc} and Ω_{arag} at a rate of -0.18 ± 0.07 decade^{-1} and -0.12 ± 0.05 decade^{-1}, respectively (Figures 7e and 7f). The record of direct measurements of pH$_{T25}$ by spectrophotometry since 2003 (Figure 5c) is not long enough to determine any trends in acidification, but these long-term changes in measured and calculated seawater CO$_2$ parameters demonstrate that the coastal ocean off Honshu, Japan, as well as subtropical zone south of the Kuroshio is being threatened by ocean acidification.

[24] Superposed on the long-term trends, cold events in winter further enhance the increase of NTCO$_2$ and decrease of saturation states of aragonite and calcite. On 19 January 2006, for example, low SST of $+13.7$°C was recorded when sample of TCO$_2$ was taken at 34°N (Figure 5f). It was 2.1°C lower than the mean of $+15.8 \pm 1.2$ (1s) °C at this site in mid January for 1994–2008, and even 1.2°C lower than that in early March ($+14.9 \pm 1.3$°C) when mean SST is usually the lowest in a year. At this time, NTCO$_2$ (2088 μmol kg^{-1}) was the highest and pH$_{T25}$ (7.905) and Ω_{arag} (2.45) were the lowest in 2002–2008 (Figures 5b, 5c, and 5e). Temperature in the mixed layer was even lower ($+13.3$°C) when CTD observation was made at this station. The thickness of mixed layer (150 m) was the deepest and temperature at the depth of 160 m below the mixed layer was the coldest (11.5°C) due to the uplifting of isotherms (Figure 4). From these observations, it is thought that the stronger turbulent mixing by cold wind together with the enhanced upwelling that was related to the ocean dynamics enhanced the entrainment of subsurface CO$_2$-rich water, and thus raised NTCO$_2$ and lowered pH and saturation states of carbonates in surface water. On the other hand, in January 2005 when the Kuroshio took a large meander path, mixed layer temperature was $+18.0$°C at 34°N (Figures 4 and 5f). It was $+2.2$°C higher than the mean in mid-January for 1994–2008. At this time, NTCO$_2$ (2013 μmol kg^{-1}) was lower and pH$_{T25}$ (8.021) and Ω_{arag} (3.08) were higher than in other winter seasons (Figures 5b, 5c, and 5e). It is known that SST in the coastal ocean tends to become higher when the Kuroshio take a large meander path [*Sugimoto and Yoshida*, 2005]. Changes in ocean dynamics associated with the Kuroshio large meander also affect carbonate chemistry and raise the carbonate saturation state in surface layer at 34°N.

[25] The difference between pCO$_2$sw and pCO$_2$air (ΔpCO$_2$) has not changed significantly for the last 25 years in the northern subtropical zone along 137°E [*Midorikawa et al.*, 2010]. Assuming that pCO$_2$sw will increase in the same rate as pCO$_2$air while NTA will keep the contemporary value, and that seasonal and interannual variations of temperature and salinity from 1994 through 2008 will repeat, we calculated the future trend of acidification. Ω_{arag} in the coastal ocean south of Honshu will decline from about 2.8 at present to 2.0 when the level of atmospheric CO$_2$ reaches 535 ppm in a normal winter (SST = 15°C). In a colder winter, such as in January 2006, or at colder sites within this zone where SST is lower than 14°C, Ω_{arag} will decline to 2.0 when the level of atmospheric CO$_2$ is no more than 500 ppm. To date, annual CO$_2$ emissions resulting from combustion of fossil fuels are increasing along a curve
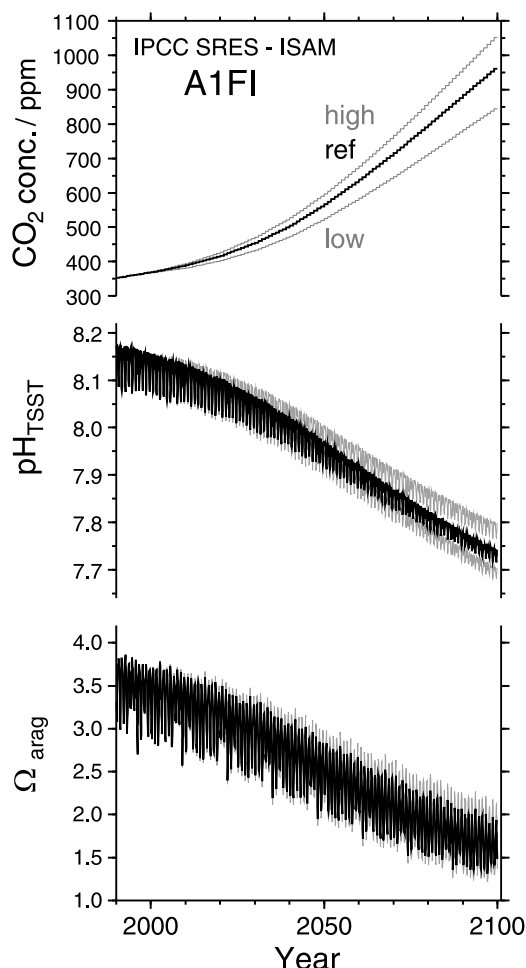
Figure 8. Trends forecasted for the end of this century according to the emission scenario A1FI from the Intergovernmental Panel on Climate Change (see http://www.grida.no/publications/other/ipcc_sr/) and seawater CO_2 parameters in the coastal ocean off the south coast of Honshu, Japan, as determined in this work: atmospheric CO_2 concentration, pH_T at in situ temperatures, and Ω_{arag}.

similar to the A1FI scenario (with intensive fossil fuel use associated with very rapid economic growth) in the Intergovernmental Panel on Climate Change's Special Report on Emissions Scenarios [*Le Quéré et al.*, 2009]. Under this scenario, Ω_{arag} could decline rapidly over the next 50 years by 0.8 to 1.0, depending on the atmospheric CO_2 concentration increase that is realized (Figure 8). Ω_{arag} could decline to 2.0 by the year 2040 under colder winter conditions, and by the year 2055 under normal winter conditions.

[26] Biological responses to ocean acidification are as yet largely unknown [*Doney et al.*, 2009]. It has been suggested that acidification enhances the production of sea grasses [*Palacios and Zimmerman*, 2007], diatoms [*Riebesell et al.*, 2007], and nitrogen-fixing cyanobacteria *Trichodesmium* [*Barcelos e Ramos et al.*, 2007] that is encountered in high abundance in surface waters of the Kuroshio and its adjacent regions [*Capone*, 1997]. In contrast, laboratory experiments have shown that, for a variety of calcareous organisms, the rate of calcification decreases as the CO_2 level increases and Ω decreases. These organisms include corals [e.g.,

Kleypas and Yates, 2009], the Pacific oyster *Crassostrea gigas* [*Gazeau et al.*, 2007], and *Gephyrocapsa oceanica* [*Riebesell et al.*, 2000] that are also seen in the region we studied and/or in the adjacent coastal basins. These experimental results suggest that the rapid decline in Ω_{calc} and Ω_{arag} as well as the increase in CO_2 predicted for the next 50 years would have a large impacts on calcareous organisms and ecosystems in the coastal ocean off of Honshu, even though Ω_{arag} and Ω_{calc} values are higher than those in the polar regions where Ω_{arag} is closer to 1.0 [*Orr et al.*, 2005]. Our conclusions on the acidification in the north of the Kuroshio also suggest its impacts on the biogeochemistry and ecosystem in the coastal basins adjacent to this region through the water exchange by tidal mixing. The progress of ocean acidification and its impacts on ecosystems and biogeochemical processes, and their possible feedback mechanisms to acidification, need to be understood by long-term monitoring in coastal zones as well as in open oceans.

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